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ARTICLE

The Coordination Behavior of Oxygen-depleted Calixarenes towards d^{10} Noble Metal Ions

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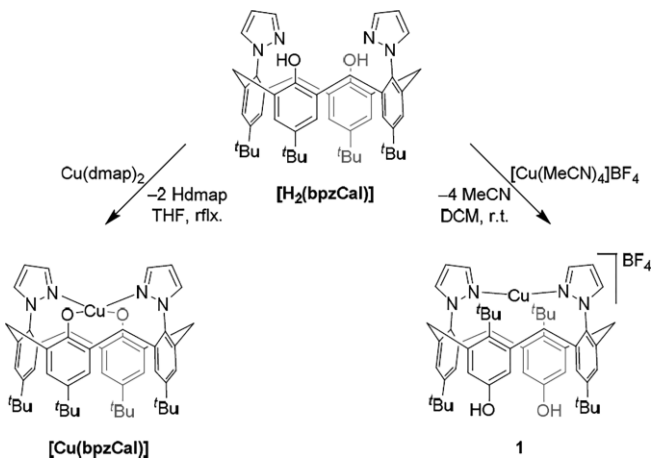
Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract. A calix[4]arene, in which two of the phenol functions are replaced by pyrazole units, [H_2(bpzCal)], was investigated as a ligand for Cu^+, Ag^+ and Au^+ ions. Using [Cu(MeCN)$_4$]BF_4 and $AgSbF_6$ as the precursors, complexes [MH_2(bpzCal)]X (M = Cu, X = BF_4; M = Ag, X = SbF_6) were formed, where the calixarene ligands adopt a *1,3-alternate* structure and the metal ions are coordinated linearly by the two pyrazolyl donors. [CuH_2(bpzCal)]BF_4 displayed a – for copper(I) complexes – unusual stability towards O_2, which is due to the steric protection of the Cu^I center. By contrast a dinuclear copper(I) complex [Cu_2(bpzCal)] that was obtained through treatment of [H_2(bpzCal)] with two equivalents of Cu(HMDS) is rather sensitive towards O_2. The preparation of a gold complex required the employment of a gold precursor, which contains one labile and one stabilizing neutral ligand, namely [(PPh_3)Au(NCMe)]SbF_6, which led to the formation of [(PPh_3)AuH_2(bpzCal)]SbF_6. In this complex [H_2(bpzCal)] acts only as a monodentate ligand for the gold center. Taken together, the results demonstrate the potential of [H_2(bpzCal)] in providing rather different coordination spheres for metal ions.

Introduction

Calixarenes are obtained in condensation reactions between phenols and aldehydes and their most prominent feature is the chalice formed by the resulting framework. Beside many other applications, they are also commonly employed in coordination chemistry as flexible and broadly variable ligands.[1] The parent calix[4]arene has four phenolate functions connected via methylene units and its metal complexes have, for instance, been utilized as mimics of oxide-supported metal sites.[2] However, given that they provide a coordination platform that contains exclusively hard oxygen donors, they have only rarely been used in biomimetic studies.[3] Recently, we have been able to show, that an oxygen-depleted calixarene, where two of the phenol functions are formally replaced by pyrazolyl functions, i.e. bispyrazolyl-*tert*-butyl-calix[4]arene ([H_2(bpzCal)], Scheme 1), provides a unique biomimetic donor sphere that resembles the one of the His_2-Tyr_2 cores found in certain enzymes.[4]



Scheme 1. Generation of the copper(II) complex [Cu(bpzCal)] and the copper(I) complex [CuH_2(bpzCal)]BF_4 (**1**) by employing the oxygen-depleted bispyrazolyl-*tert*-butyl-calix[4]arene [H_2(bpzCal)] [dmap = 1-(dimethylamino)-2-propanolate anion].

Hence, [Cu(bpzCal)], generated from the ligand precursor through treatment with Cu(dmap)$_2$ (Scheme 1), was found to represent a structural and functional model[5] for the copper protein galactose oxidase (GO), which in nature catalyzes the oxidation of primary alcohols to the corresponding aldehydes using O_2. Like the enzyme, the model [Cu(bpzCal)] can be singly oxidized to yield a phenoxyl radical coordinating to the copper center, mimicking the active state of the GO.[5] The oxidized complex proved capable of converting benzyl alcohol to the corresponding aldehyde, like the GO does, but through a different mechanism involving two equivalents of the complex. The latter were necessary, as the oxidation potential of [Cu(bpzCal)] is evidently not sufficiently high for a cooperation of the copper ion in the alcohol oxidation, that would lead

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to a copper(I) state capable of activating O_2 in the next step of the catalytic cycle. We were interested in the reason for the low potential for the Cu^{I}/Cu^{II} redox pair and therefore investigated the behavior of $[H_2(bpzCal)]$ towards copper(I) sources. Herein we describe the results that led us to also investigate the complexation of Ag^+ and Au^+ for comparison.

Results and Discussion

A solution of $[H_2(bpzCal)]$ in dichloromethane was reacted with a solution of $[Cu(MeCN)_4]BF_4$ in the same solvent at room temperature (Scheme 1).

After stirring for an hour the solvent was removed and a ^1H NMR spectrum recorded subsequently showed a signal set with a pattern that pointed to a C_{2v} symmetry of the ligand; for instance, two singlets were observed for the four *tert*-butyl residues (see Figure S1, Supporting Information). The signal for the phenolic OH groups at $\delta = 11.00$ ppm did not disappear but shifted to 4.53 ppm, indicating that no deprotonation had occurred and that the environment had significantly changed. Layering of a dichloromethane solution of the product with *n*-hexane led to the growth of crystals that were suitable for a single-crystal X-ray diffraction study. It revealed the structure of the complex $[CuH_2(bpzCal)]BF_4$ (**1**) as shown in Figure 1.

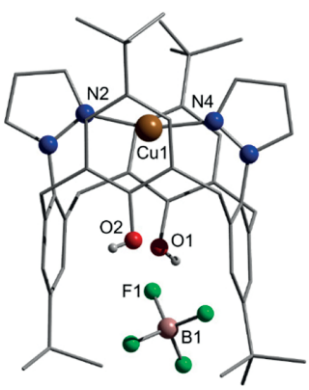


Figure 1. The molecular structure of **1**; selected bond lengths /Å and angles /°: Cu1–N2 1.871(2), Cu1–N4 1.869(2), N2–Cu1–N4 161.48(11). Hydrogen atoms (apart from the OH protons) and co-crystallized solvent molecules are omitted for clarity.

The calixarene ligand is found in a *1,3-alternate* conformation – formed through a rotation of the phenolic units by 180° around the methylene linkers – so that the oxygen atoms are averted from the copper(I) ion, which is coordinated by the two pyrazolyl donors in a nearly linear fashion (N–Cu–N = 161.48°); a tetrafluoroborate counterion resides in the cavity below the copper ion. The structure matches very well the observations made by ^1H NMR spectroscopy. Hence, apparently, the Lewis acidity of the copper ion is sufficiently compensated by the pyrazolyl donors and a further interaction with the phenol donors is not favorable. A single electron reduction of [Cu(bpzCal)] would lead to such a situation, and this explains that its oxidation potential is not sufficiently high to promote alcohol oxidation.

Although without phenol coordination the Cu-His_2-Tyr_2 core of the GO is not adequately mimicked in **1**, we were nonetheless interested in how far it is capable of reacting with O_2 (as the copper(I) state of the GO). Remarkably, **1** turned out to be stable towards dioxygen in common solvents for more than 24 h. There is a small number of two-coordinated copper(I) complexes in the literature which show a comparable stability towards dioxygen. In some cases the linear coordination sphere was discussed to be responsible, in other cases electronic factors or rigid, prearranged binding.[6] For instance, a complex with a copper(I) center coordinated linearly by two imidazolyl donors attached via ether linkages to a calixarene framework also showed an exceptional stability towards O_2.[6c] However, we believe that in case of **1** steric shielding is responsible. The two aryl rings of the inverted phenol functions and their *tert*-butyl groups are embedding the copper(I) ion, so that a contact with any substrate is hardly possible as illustrated in the space-filling model depicted in Figure 2.

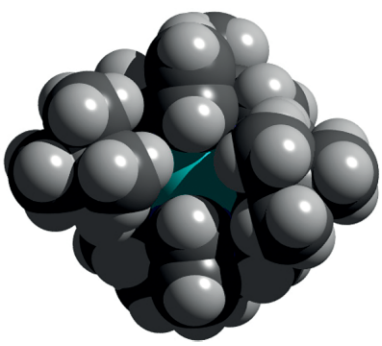


Figure 2. Space-filling model of **1** viewed from the top with the *tert*-butyl groups of the phenol entities pointing towards the spectator. The copper ion is colored in blue.

When a copper(I) precursor with a basic ligand, namely $[Cu(HMDS)]_4$ (HMDS = hexamethyldisilazide) was used at elevated temperatures in complexation reactions with $[H_2(bpzCal)]$, the latter took a different course. For a complete complexation of $[H_2(bpzCal)]$ then two equivalents were required (see Figure 3), and the disappearance of the OH signals in the ^1H NMR spectrum indicated the full deprotonation of the ligand precursor, leading to a formula $[Cu_2(bpzCal)]$ (**2**). According to the ^1H NMR spectrum the product, which was formed selectively with successive addition of Cu(HMDS), has a C_{2v} symmetry. Unfortunately, it was not possible to crystallize the complex in order to get more detailed information on its structure. Notably, it is rather sensitive towards O_2, which causes the formation of $[Cu^{II}(bpzCal)]$.

Having experienced the formation of different complexes in dependence on the copper(I) source, we were interested to compare the complexation of silver(I). Hence, $[H_2(bpzCal)]$ was treated with $AgSbF_6$ in dichloromethane. After removal of all volatiles the resulting product showed a ^1H NMR spectrum that was rather similar to the one of **1**, thus pointing to a formula $[AgH_2(bpzCal)]SbF_6$ (**3**), (Scheme 2), which was confirmed by an X-ray structure analysis of single crystals (Figure 4).

The molecular structure of **3** essentially corresponds to the one determined for **1**. Due to the larger ionic radius of Ag^+ as compared to Cu^+ the Ag–N distances are in average 0.237 Å

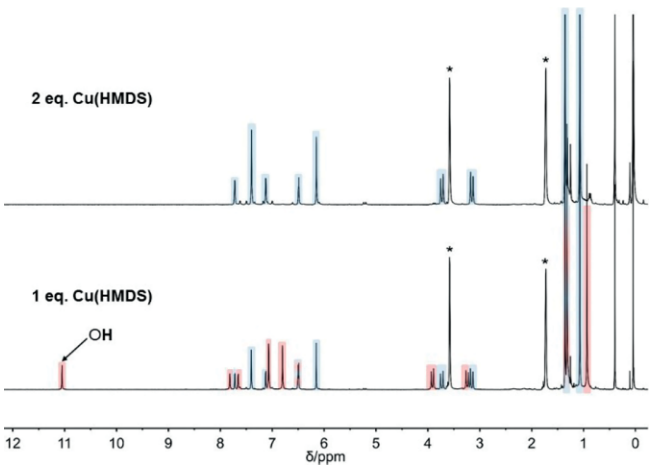
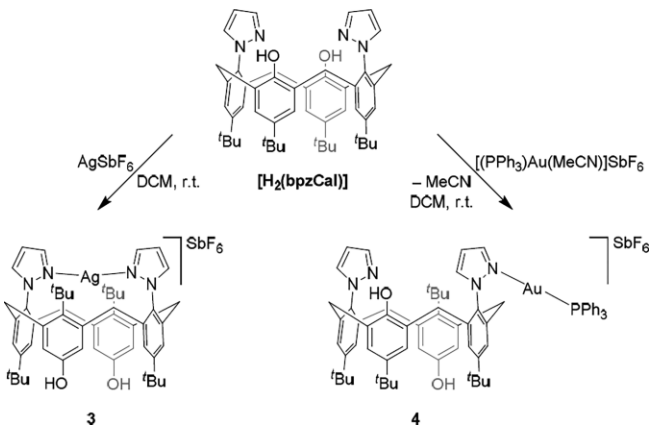


Figure 3. ^{1}H NMR spectra recorded after the addition of one and two equivalents of Cu(HMDS) to a solution of [H_2(bpzCal)] (red) in [D_8]THF (*) illustrating the clean formation of **2** (blue).



Scheme 2. Generation of the silver(I) complex [AgH_2(bpzCal)] (**3**) and the gold(I) complex [(PPh_3)AuH_2(bpzCal)]SbF_6 (**4**) by employing the oxygen-depleted bispyrazolyl-*tert*-butyl-calix[4]arene [H_2(bpzCal)].

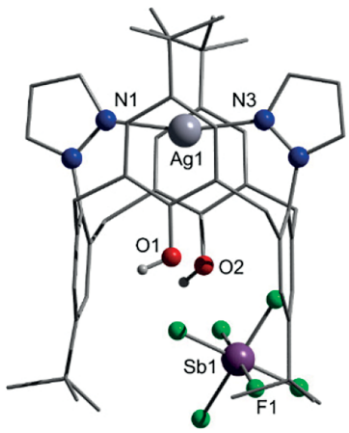


Figure 4. The molecular structure of **3**; selected bond lengths /Å and angles /°: Ag1–N1 2.109(4), Ag1–N3 2.105(4), N1–Ag1–N3 165.34(14). Hydrogen atoms (apart from the OH protons) are omitted for clarity.

longer than the Cu–N distances. Naturally, this posed the question whether gold(I) ions could be accommodated this way in the binding pocket, too.

Addition of AuCl, Au(SMe_2)Cl, Au(PPh_3)Cl or Au(PPh_3)Me to solutions of [H_2(bpzCal)] in dichloromethane did not lead to any reaction. Although [H_2(bpzCal)] as a chelating ligand should lead to more stable complexes, apparently substitution of the monodentate ligands at the gold centers, especially those bound covalently, is unfavorable. There are a few gold complexes known, which contain weakly bound ligands and therefore are conceivable as precursors. Typically, they are rather unstable and have to be prepared in situ. For first complexation studies with [H_2(bpzCal)] we have selected [Au(-MeCN)$_2$]SbF_6, which was prepared in CD_2Cl_2 for an NMR tube experiment by reacting AuCl with $AgSbF_6$. This immediately led to the precipitation of AgCl and the resulting solution was filtered into a CD_2Cl_2 solution of [H_2(bpzCal)]. However, a black solid precipitated and the ^{1}H NMR recorded subsequently did not reveal a uniform reaction process with formation of a defined product; some of the signals observed were not even assignable to any type of calixaren-based compound. Apparently, the highly reactive precursor complex [Au(-MeCN)$_2$]SbF_6 has decomposed the ligand precursor, possibly through insertion into C–C bonds.

Hence, [(PPh_3)Au(MeCN)]SbF_6 was employed next, which contains one rather labile acetonitrile ligand but also a stabilizing phosphine ligand. Its reaction with [H_2(bpzCal)] did not lead to a black solid but to a clear solution, the NMR spectrum of which pointed to a clean conversion to a product with C_s symmetry (three signals for the *tert*-butyl groups in the ratio 2:1:1, see Figure S3, Supporting Information) and thus to a coordination of only one pyrazolyl donor. This inference fits to the finding of only one signal at δ = 30.30 ppm in the ^{31}P NMR spectrum, corresponding to a gold-bound phosphine ligand. Altogether this suggested the formula [(PPh_3)AuH_2(bpzCal)]SbF_6 (**4**), for the product (Scheme 2), and an X-ray diffraction analysis with crystals grown by layering a dichloromethane solution with *n*-hexane confirmed this conclusion (Figure 5).

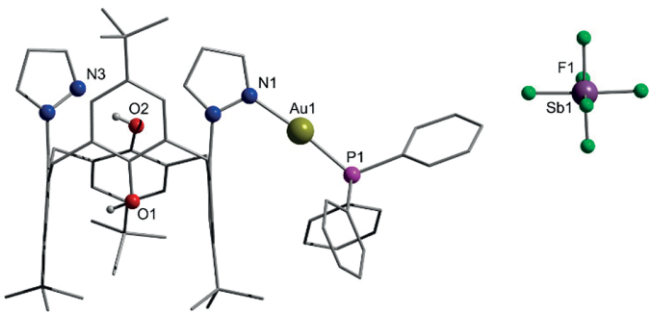


Figure 5. The molecular structure of **4**; selected bond lengths /Å and angles /°: Au1–N1 2.056(3), Au1–P1 2.2381(8), N1–Au1–P1 173.40(8). Hydrogen atoms (apart from the OH protons) are omitted for clarity.

The calixarene acts only as a monodentate ligand via the pyrazolyl function that coordinates the gold ion. The second pyrazolyl donor still forms a hydrogen bridge to one of the phenolic OH groups (O2) that is also present (doubly) in the structure of [H_2(bpzCal)]. Apparently, the energy needed for breaking-up this bond and the Au–P bond is higher than the

energy released by coordination of the second pyrazole entity. Interestingly, the second phenol unit again has flipped so that the OH group is pointing away from the residual donors, leading to a *partial-cone* conformation.

Conclusions

Investigating the coordination behavior of [H_2(bpzCal)] towards monovalent d^{10} transition metal ions have revealed two new coordination modes for this ligand. In the absence of bases Cu^+ and Ag^+ are bound linearly by the two pyrazolyl units, while the two phenol functions remain protonated and flip into the opposite direction. In consequence their *tert*-butyl groups bury the metal ions such that the copper(I) complex behaves inert towards O_2. The fact that unlike the copper(II) complex, which features a *cone* conformation, the copper(I) complex prefers a *1,3-alternate* structure explains that reduction of the copper(II) in [Cu^{II}(bpzCal)] only occurs at comparatively negative potentials and that it consequently cannot play an active role in biomimetic oxidation cycles. Using a basic copper precursor a deprotonation of the two phenol units was observed leading to a C_{2v} symmetric complex [Cu_2(bpzCal)] that unfortunately could not be characterized structurally. In combination with gold(I) a yet different coordination mode of [H_2(bpzCal)] was observed: a monodentate binding via just one pyrazole donor.

In future work we will try to exploit the unreacted phenol functions of these noble metal complexes to create functional heterobimetallic compounds.

Experimental Section

General Considerations: All manipulations were carried out in an argon atmosphere using conventional Schlenk techniques or in gloveboxes with either dinitrogen or argon atmospheres maintained below 1 ppm of O_2 and H_2O. Glassware was heated under vacuum using a heat gun at 650 °C prior to use. All solvents used for reactions were either dried with a MBraun solvent purification system (SPS) (THF was additionally distilled from Solvona®) or by using standard literature methods. Degassing was performed by bubbling argon through the solvent for 20 min. Deuterated solvents for NMR were dried by storing over 3 Å molecular sieves, degassed by freeze-pump-thaw technique (3 cycles) and stored in a glove box. NMR spectra were recorded on a Bruker AVANCE II 300 spectrometer. Chemical shifts are referenced to the residual proton signal of the solvent.[7] IR spectra were recorded in an argon filled glovebox on a Bruker ALPHA spectrometer with an ATR sampling unit. Electrospray ionization (ESI) mass spectra were obtained on an Agilent Technologies 6210 Time-of-Flight LC-MS instrument. Elemental analyses were performed with a HEKA Euro 3000 elemental analyzer.

[$Cu(MeCN)_4$]BF_4 was purchased from TCI, $AgSbF_6$ from Alfa Aesar and (PPh_3)AuCl from ABCR; the reagents were used as received. [H_2(bpzCal)],[8] [Cu(HMDS)]$_4$[9] and [(PPh_3)Au(MeCN)]SbF_6[10] were prepared according to literature procedures.

Synthesis of [CuH_2(bpzCal)]BF_4 (1): [H_2(bpzCal)) (35.0 mg, 46.7 µmol, 1 equiv.) was dissolved in dichloromethane (10 mL) and a suspension of [$Cu(MeCN)_4$]BF_4 (14.7 mg, 46.7 µmol, 1 equiv.) in dichloromethane (5 mL) was added. After stirring for 1 h at room temperature the reaction mixture was filtered and the volume of the filtrate reduced to 5 mL. Addition of *n*-hexane (15 mL) led to the precipitation of [CuH_2(bpzCal)]BF_4, **1** (34.0 mg, 37.8 µmol, 81 % yield) in form of a colorless solid that was dried under high vacuum. Single crystals, which were suitable for an X-ray diffraction analysis, could be grown by layering a dichloromethane solution with *n*-hexane. **^{1}H NMR** (300 MHz, DCM-d_2, 20 °C): δ = 7.55 (s, 6 H, $^5H_{pz}$+H_{Ar}), 7.28 (d, ^2J(H,H) = 1.8 Hz, 2 H, $^3H_{pz}$), 6.72 (t, $^2J_{H,H}$ = 2.2 Hz, 2 H, $^4H_{pz}$), 6.27 (s, 4 H, H_{Ar}), 4.53 (s, 2 H, OH), 3.88 (d, $^1J_{H,H}$ = 15.3 Hz, 4 H, $^{exo}CH_2$), 3.26 (d, $^1J_{H,H}$ = 15.2 Hz, 4 H, $^{endo}CH_2$), 1.37 (s, 18 H, $C(CH_3)_3$), 1.12 (s, 18 H, $C(CH_3)_3$) ppm. **ATR-IR**: $\tilde{\nu}$ = 3517 (w), 3460 (w), 3132 (w), 2954 (w), 2904 (w), 2866 (w), 1598 (w), 1522 (w), 1512 (w), 1478 (m), 1438 (w), 1410 (w), 1393 (w), 1363 (w), 1327 (w), 1203 (w), 1112 (w), 1084 (s), 1056 (vs), 1035 (s), 974 (w), 954 (w), 920 (w), 876 (w), 822 (w), 806 (w), 762 (vs), 743 (w), 734 (w), 694 (w), 637 (w), 628 (w), 619 (w), 607 (w), 578 (w), 541 (w), 520 (w), 486 (w), 468 (w), 452 (w), 418 (w) cm^{-1}. **ESI-MS** (DCM, +MS): *m*/*z* = 811.4028 $[M–BF_4]^+$ (calcd. 811.4012). . $C_{50}H_{60}N_4O_2CuBF_4$ (899.41 g·mol^{-1}); C 66.52 (calcd. 66.77); H 7.04 (6.72); N 5.97 (6.23) %.

Synthesis of [Cu_2(bpzCal)] (2): (NMR tube experiment): [H_2(bpzCal)] (10.0 mg, 13.4 µmol, 1 equiv.) was dissolved in [D_8]THF (0.5 mL) and a suspension of [Cu(HMDS)]$_4$ (6.0 mg, 6.7 µmol, 2 equiv.) in [D_8]THF (0.5 mL) was added. After heating at 68 °C for 12 h an NMR spectrum was recorded. **^{1}H NMR** (300 MHz, [D_8]THF, 20 °C): δ = 7.72 (d, $^1J_{H,H}$ = 2.1 Hz, 2 H, $^5H_{pz}$), 7.40 (s, 4 H, H_{Ar}), 7.13 (d, $^1J_{H,H}$ = 1.7 Hz, 2 H, $^3H_{pz}$), 6.49 (t, $^2J_{H,H}$ = 2.2 Hz, 2 H, $^4H_{pz}$), 6.15 (s, 4 H, H_{Ar}), 3.73 (d, $^1J_{H,H}$ = 14.6 Hz, 4 H, $^{exo}CH_2$), 3.16 (d, $^1J_{H,H}$ = 15.0 Hz, 4 H, $^{endo}CH_2$), 1.36 (s, 18 H, $C(CH_3)_3$), 1.07 (s, 18 H, $C(CH_3)_3$) ppm.

Synthesis of [AgH_2(bpzCal)]SbF_6 (3): [H_2(bpzCal)] (35.0 mg, 46.7 µmol, 1 equiv.) was dissolved in dichloromethane (10 mL) and a solution of $AgSbF_6$ (16.1 mg, 46.7 µmol, 1 equiv.) in dichloromethane (5 mL) was added. After stirring for 1 h at room temperature the colorless reaction mixture was filtered and the volume of the filtrate reduced to 5 mL. The addition of *n*-hexane (15 mL) led to the precipitation of [AgH_2(bpzCal)]SbF_6, **3** (44.8 mg, 38.9 µmol, 83 % yield) in form of a colorless solid that was dried under high vacuum. Single crystals, which were suitable for an X-ray diffraction analysis, could be grown by layering a dichloromethane solution with *n*-hexane. **^{1}H NMR** (300 MHz, DCM-d_2, 20 °C): δ = 7.57 (s, 6 H, $^5H_{pz}$+H_{Ar}), 7.32 (d, $^2J_{H,H}$ = 2.1 Hz, 2 H, $^3H_{pz}$), 6.77 (s, 2 H, $^4H_{pz}$), 6.32 (s, 4 H, H_{Ar}), 4.56 (s, 2 H, OH), 3.89 (d, $^1J_{H,H}$ = 15.0 Hz, 4 H, $^{exo}CH_2$), 3.26 (d, $^1J_{H,H}$ = 15.3 Hz, 4 H, $^{endo}CH_2$), 1.39 (s, 18 H, $C(CH_3)_3$), 1.15 (s, 18 H, $C(CH_3)_3$) ppm. **ATR-IR**: $\tilde{\nu}$ = 3565 (w), 3501 (w), 2956 (w), 2907 (w), 2869 (w), 1597 (w), 1511 (w), 1477 (m), 1434 (w), 1403 (w), 1364 (w), 1326 (w), 1297 (w), 1281 (w), 1196 (m), 1116 (w), 1072 (w), 1032 (w), 966 (w), 953 (w), 921 (w), 881 (w), 823 (w), 808 (w), 775 (m), 761 (m), 744 (w), 733 (w), 654 (vs), 619 (m), 605 (w), 575 (w), 543 (w), 518 (w), 493 (w) cm^{-1}. **ESI-MS** (DCM, +MS): *m*/*z* = 855.3797 $[M–SbF_6]^+$ (calcd. 855.3767). $C_{50}H_{60}N_4O_2AgSbF_6$ (1150.80 g·mol^{-1}); C 56.01 (calcd. 56.36); H 6.44 (6.13); N 4.68 (4.87) %.

Synthesis of [(PPh_3)AuH_2(bpzCal)]SbF_6 (4): [H_2(bpzCal)] (35.0 mg, 46.7 µmol, 1 equiv.) was dissolved in dichloromethane (10 mL) and a solution of [(PPh_3)Au(MeCN)]SbF_6 (34.4 mg, 46.7 µmol, 1 equiv.) in dichloromethane (5 mL) was added. After stirring for 1 h at room temperature the colorless reaction mixture was filtered and the volume of the filtrate reduced to 5 mL. The addition of *n*-hexane (15 mL) led to the precipitation of [(PPh_3)AuH_2(bpzCal)]SbF_6, **4** (60.2 mg, 40.1 µmol, 86 % yield).in form of a colorless solid that was dried under

high vacuum. Single crystals, which were suitable for an X-ray diffraction analysis, could be grown by layering a dichloromethane solution with *n*-hexane. **^{1}H NMR** (300 MHz, DCM-d_2, 20 °C): δ = 7.95 (d, $^2J_{H,H}$ = 2.3 Hz, 1 H, H_{pz}), 7.88 (d, $^2J_{H,H}$ = 2.1 Hz, 1 H, H_{pz}), 7.69 (d, $^2J_{H,H}$ = 2.3 Hz, 1 H, H_{pz}), 7.67–7.61 (m, 3 H, *p*-H_{PPh3}), 7.64 (d, $^2J_{H,H}$ = 2.1 Hz, 1 H, H_{pz}), 7.56–7.51 (m, 6 H, *o*-H_{PPh3}), 7.33–7.26 (m, 8 H, *m*-H_{PPh3}+OH), 7.07 (s, 2 H, H_{Ar}), 6.87 (s, 2 H, H_{Ar}), 6.82 (s, 2 H, H_{Ar}), 6.81 (s, 2 H, H_{Ar}), 6.66 (t, $^2J_{H,H}$ = 2.1 Hz, 1 H, H_{pz}), 6.61 (t, $^2J_{H,H}$ = 2.1 Hz, 1 H, H_{pz}), 3.62 (d, $^1J_{H,H}$ = 14.9 Hz, 2 H, $^{exo}CH_2$), 3.55 (d, $^1J_{H,H}$ = 14.9 Hz, 2 H, $^{endo}CH_2$), 3.48 (d, $^1J_{H,H}$ = 13.8 Hz, 2 H, $^{endo}CH_2$), 3.26 (d, $^1J_{H,H}$ = 13.8 Hz, 2 H, $^{endo}CH_2$), 1.29 (s, 18 H, $C(CH_3)_3$), 1.10 (s, 9 H, $C(CH_3)_3$)), 0.74 (s, 9 H, $C(CH_3)_3$) ppm. **^{31}P{^{1}H} NMR** (121.5 MHz, DCM-d_2, 20 °C): δ = 30.30 ppm. **ATR-IR**: $\tilde{\nu}$ = 3529 (w), 3158 (w), 2961 (w), 2907 (w), 2867 (w), 1594 (w), 1513 (w), 1479 (m), 1438 (w), 1407 (w), 1364 (w), 1330 (w), 1307 (w), 1284 (w), 1268 (w), 1234 (w), 1206 (w), 1164 (w), 1104 (w), 1076 (w), 1057 (w), 1030 (w), 999 (w), 976 (w), 956 (w), 919 (w), 905 (w), 876 (w), 823 (w), 805 (w), 767 (m), 751 (m), 713 (w), 693 (m), 653 (vs), 625 (m), 590 (w), 570 (w), 544 (m), 508 (m), 497 (m), 456 (w), 437 (w) cm^{-1}. **ESI-MS** (DCM, +MS): *m/z* = 1207.5341 [M–SbF_6]$^+$ (calcd. 1207.5293). $C_{50}H_{60}N_4O_2AuPC_{18}H_{15}SbF_6$ (1502.19 g·mol^{-1}); C 57.11 (calcd. 57.57); H 6.07 (5.70); N 3.40 (3.73) %.

Supporting Information (see footnote on the first page of this article): X-ray data, NMR and IR spectra

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